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# An Investigation of Cubane Rearrangements

Theses of the Doctoral (Ph. D.) Dissertation

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# Introduction

Transition metal catalyzed skeletal rearrangements of strained systems have been known since the 1970s. Among these, one of the first described examples is the transformation of cubane (**1a**, R = H) to cuneane (**2a**, R = H). Silver(I) perchlorate or palladium(II) chloride catalyzed this rearrangement which, in the case of substituted cubanes, afforded mixtures of cuneane isomers [Figure 1]. According to the proposed mechanism, oxidative addition of the metal ion to a C–C bond is followed by carbonium ion formation and rearrangement.

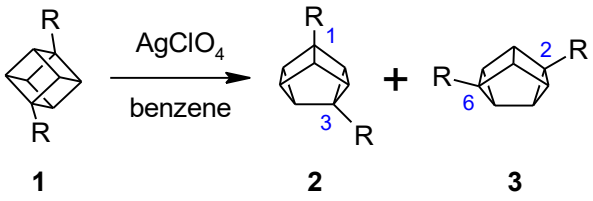


**Figure 1. Silver-catalyzed rearrangement of cubanes**

Lithium(I) with a weakly coordinating carborane anion was also used to induce a skeletal rearrangement on cubane and some analogous compounds, however, these rearrangements presumably follow a mechanism different from the transition metal catalyzed transformation. Apart from Ag(I), Pd(II) and Li(I), no other species was found to induce a rearrangement to cuneane. Theoretical studies suggest that protonation or single electron transfer oxidation of cubane may also result in a rearrangement leading either to cuneane or to pentalenes, but experimental proof seems to be controversial.

Ring opening reactions affording tricyclooctadiene or cyclooctatetraene, have also been reported. Conversion of cubane to *syn*-tricyclooctadiene is induced by rhodium(I) ions or lithium di(*iso*-propyl)amide. This intermediate can be converted to cyclooctatetraene upon heating. Direct thermal ring opening of cubanes is also possible without catalyst and even without solvent.

The proposed ionic mechanism of the transition metal catalyzed rearrangement suggests that rearrangement to cuneane is favored by polar media. However, the rearrangement of cubanes was not studied in polar solvents previously. Also no detailed study has been devoted to the conditions of the rearrangement.

My aim was to investigate how solvent polarity, temperature, and the concentration of the silver(I) ion or other additives affect reaction rate and product/isomer distribution. Whereas

previous studies have been dealt with less polar derivatives, I have chosen a water-soluble model compound, cubane-1,4-dicarboxylic acid (**1b**, R = COOH).

The interesting complex of cubane and $C_{60}$ fullerene, recently discovered by *Pekker et al.*, has a rotor-stator phase at room temperature and polymerizes at higher temperatures with the rearrangement of the cubane skeleton. Examination of this cocrystal might provide new information on the bond structure, noncovalent interactions and rearrangements of cubanes. The compound might be a precursor of novel nanocomposites and molecular machines. I participated in the study of the phase transitions of the cubane–fullerene complex in cooperation with the research group of *Sándor Pekker* (Hungarian Academy of Sciences, Wigner Research Centre for Physics).

# Results and Conclusions

## 1. Study of the rearrangement of cubane-1,4-dicarboxylic acid

### 1.1. The rearrangement of cubane-1,4-dicarboxylic acid can be made chemoselective

Cubane-1,4-dicarboxylic acid (**1b,** R = COOH) rearranges chemoselectively to cuneane-2,6-dicarboxylic acid (**3b**, R = COOH) in water in the presence of silver nitrate. No other, 1,3-disubstituted isomer (**2b**, R = COOH) is formed.

### 1.2. Determination of the minimal effective concentration of the catalyst

The minimal effective concentration of the silver nitrate catalyst is 0.0001 equiv relative to the cubane diacid.

### 1.3. Rearrangement takes place with no catalyst added

Rearrangement also occurs when no silver ions are added. Although deionized, conductivity grade water and purified materials were used, obviously the silver(I) concentration could not be reduced to ‘zero’ – ICP-MS analysis of the samples showed that the amount of residual silver(I) was three orders of magnitude lower than the minimal effective catalytic concentration. Therefore no catalytic effect can be attributed to silver(I) ions in such low concentrations.

### 1.4. Solvent-induced rearrangement occurs in polar, protic solvents

The silver-free rearrangement of cubane-1,4-dicarboxylic acid takes place only in polar, protic media. In other solvents only slow cage decomposition or ring opening to cyclooctatetraene-1,4-dicarboxylic acid was observed.

### 1.5. The rearrangement proceeds via the semi-dissociated form of the cubane diacid

The solvent-induced rearrangement can be accelerated by adding 1 equiv of base (e. g. potassium hydroxide). Strongly acidic media inhibited cuneane formation as it protonates the dissociated forms of the diacid. Also no rearrangement took place when the diacid was converted to bis(dimethyl amide) to prevent dissociation. Addition of more than 2 equiv of base also prevented rearrangement (complete dissociation). Experimentally obtained pH dependence of the conversion to cuneane [Figure 2] is in correlation with the calculated species distribution in the solution [Figure 3]. Maximum conversion corresponds to the maximum concentration of the semi-dissociated form, hydrogen cubane-1,4-dicarboxylate (**1b'**) [Figure 4].

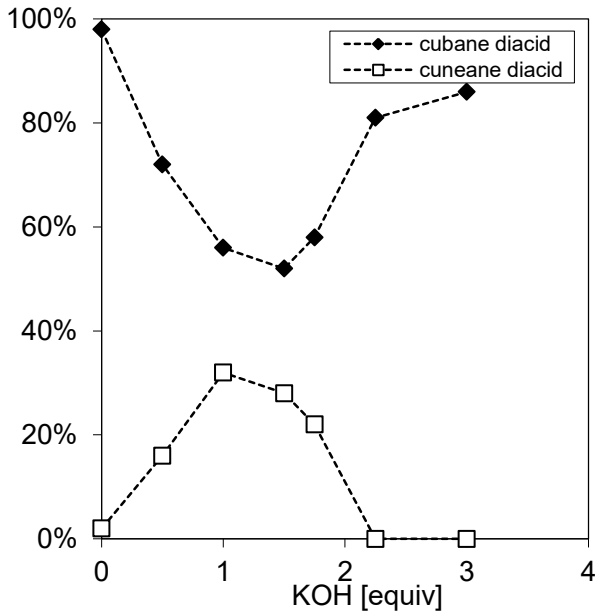


**Figure 2. The effect of added KOH on the rearrangement of cubane-1,4-dicarboxylic acid**

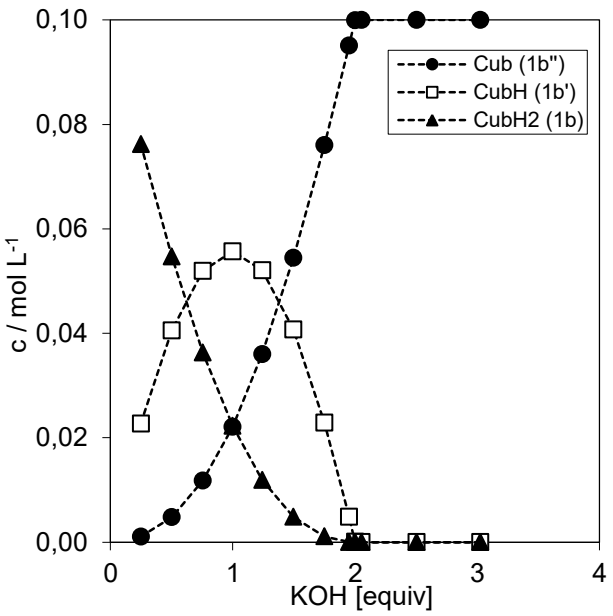


**Figure 3. The effect of added KOH on the calculated species distribution in solutions of cubane-1,4-dicarboxylic acid**

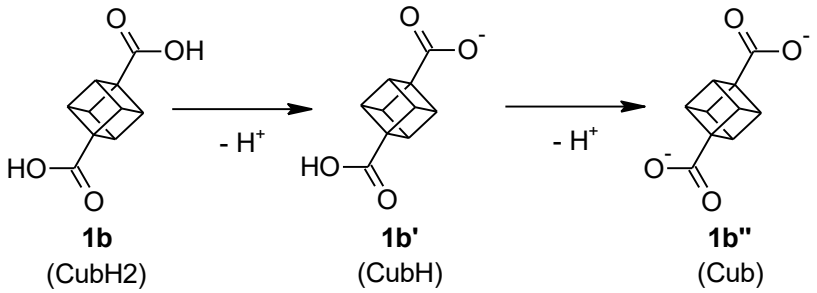


**Figure 4. Cubane-1,4-dicarboxylic acid and its dissociated forms**

### 1.6. The optimal temperature for cuneane formation is around 135 °C

Under 100 °C the rearrangement is very slow. Elevating the temperature resulted in higher cuneane yields but that is limited by the decomposition of cuneane-2,6-dicarboxylic acid and the thermal ring opening of the starting cubane dicarboxylic acid to cyclooctatetraene diacid which is favored at higher temperatures.

### 1.7. No cuneane – cyclooctatetraene rearrangement was observed

It was suggested by a previous study that cuneanes may rearrange to cyclooctatetraenes upon heating. However, cuneane-2,6-dicarboxylic acid did not rearrange such way neither in protic nor in aprotic media nor under solvent-free conditions, only slow decomposition was observed, affording an insoluble tarry material.

### 1.8. A mechanism for the solvent-induced rearrangement is proposed

In order to get a better picture on the mechanism of the metal-free rearrangement of cubane-1,4-dicarboxylic acid, quantum chemical calculations were done at B3LYP/6-31g(d) level. Two transition states were identified on the potential energy surface (PES) of the reaction. However, the second TS is avoided by the reaction path, as the two enantiomeric cuneane diacids can be reached through a branching point. Based on the experimental data and the results of calculations a mechanism is proposed for the solvent-induced rearrangement of cubane-1,4-dicarboxylic acid [Figure 5].

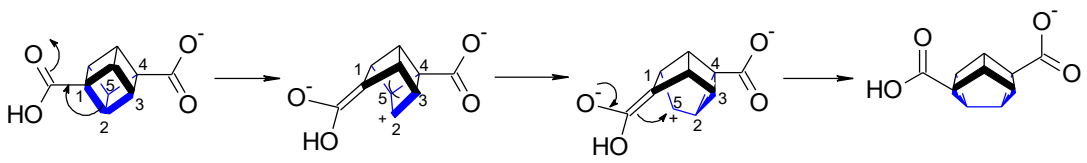

**Figure 5. Proposed mechanism of the rearrangement of hydrogen cubane-1,4-dicarboxylate**

### 1.9. No cuneane products are formed from other cubane carboxylic acids in similar conditions

Slow cage decomposition, ring opening to the corresponding cyclooctatetraene derivative or no reaction occurred in the attempted rearrangement of cubane monocarboxylic acid, cubane-1,2,4-tricarboxylic acid, cubane-1,2,4,7-tetracarboxylic acid and two homologues of cubane-1,4-dicarboxylic acid.

## 2. Phase transitions of cubane – fullerene cocrystals

### 2.1. NMR study of the cocrystals

$^{13}C$ NMR spectrum and spin–lattice relaxation time was investigated in fullerene–cubane. Reorientation motion of fullerene molecules was found to be fast on the NMR timescale even in the orientationally ordered phase. The activation barrier of the reorientation was found to be lower in the presence of cubane than in pure $C_{60}$ fullerene.

### 2.2. XRDS and INS study of the cocrystals

XRDS (X-Ray Diffuse Scattering) measurements confirmed that an important disorder remains in the fullerenes' orientations in the orientationally ordered phase below 140 K. INS (Inelastic Neutron Scattering) measurements confirmed the existence of the rotor-stator phase at room temperature. Below 140 K no change was found in fullerenes' orientations – no rotation, only libration occurs.

### 2.3. IR study of the cocrystals

Investigating the pressure dependence of the IR spectrum of $C_{60} \cdot C_8H_8$ revealed that phase transition to the orientationally ordered phase can be achieved by not only cooling but high hydrostatic pressure.

# Publications

## Research articles

[1] G. Durkó, I. Jalsovszky, Solvent-induced, selective rearrangement of hydrogen cubane-1,4-dicarboxylate to hydrogen cuneane-2,6-dicarboxylate, *Tetrahedron* **2013**, *69*, 5160–5163.

[2] E. A. Francis, G. Durkó, I. Jalsovszky, G. Klupp, K. Kamarás, É. Kováts, S. Pekker, C. A. Kuntscher, Phase transitions in $C_{60} \cdot C_8H_8$ under hydrostatic pressure *Phys. Stat. Sol. B* **2012**, *249*, 2596–2599.

[3] C. Bousige, S. Rols, J. Cambedouzou, B. Verberck, S. Pekker, É. Kováts, G. Durkó, I. Jalsovszky, E. Pellegrini, P. Launois, Lattice dynamics of a rotor-stator molecular crystal: Fullerene-cubane $C_{60} \cdot C_8H_8$ *Phys. Rev. B* **2010**, *82*, 195413.

[4] P. Matus, M. Bokor, G. Kriza, É. Kováts, S. Pekker, A. Domján, G. Durkó, I. Jalsovszky, $^{13}C$ NMR investigation of fullerene-cubane $C_{60} \cdot C_8H_8$ cocrystals, *Phys. Stat. Sol. B* **2009**, *246*, 2764–2766.

## Presentations

[5] G. Durkó, I. Jalsovszky: 1,3-bisz(acetoximetil)-kuneán előállítása 1,4-bisz(acetoximetil)-kubán szelektív átrendeződésével (Preparation of 1,3-bis(acetoxymethyl)-cuneane by the selective rearrangement of 1,4-bis(acetoxymethyl)-cubane), *MKE Vegyészkonferencia (Annual Meeting of the Hungarian Chemical Society),* Hajdúszoboszló, **2013** (poster, in Hungarian)

[6] G. Durkó, Ö. Farkas, I. Jalsovszky: A kubánváz átrendeződése vízben (The rearrangement of cubane skeleton in aqueous media), *MKE 1. Nemzeti Konferencia (1st National Conference of the Hungarian Chemical Society),* Sopron, **2011** (in Hungarian)

[7] G. Durkó, Ö. Farkas, I. Jalsovszky: A kubánváz savkatalizált átrendeződése (Acid-catalyzed rearrangement of the cubane skeleton), *MTA Elméleti Szerves Kémiai Munkabizottság előadói ülése (Meeting of the Theoretical Organic Chemistry Workgroup of the Hungarian Academy of Sciences),* Budapest, **2010** (in Hungarian)